

JAPANESE

[JP,11-080395,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL  
FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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## **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a porous membrane and the separator for nonaqueous electrolyte batteries.

[0002]

[Description of the Prior Art]Practical use is presented with the cell of various types, and a porosity film, the nature film of nonporous, a nonwoven fabric, paper, etc. are proposed as a separator for cells suitable for each. The characteristics, such as compatibility (wettability) with an electrolysis solution and solution retention, low electrical resistance and high breathability, a high mechanical strength, and chemical stability, are required of the separator for these cells. Among these characteristics, with regards to the discharge

characteristic of a cell, compatibility with an electrolysis solution, solution retention, electrical resistance, and breathability are called for in order to make movement of the ion in a cell reaction easy. A mechanical strength is the characteristic called for in order to reduce generating of the internal short circuit by the fracture of the separator in the fabrication process of a cell, etc., etc. Since the separator for cells is exposed to the oxidation and the reducing atmosphere inside a cell, it is necessary to use a chemically stable material which cannot cause decomposition, a reaction, etc. easily, and polyolefine and fluorine system polymer are used abundantly from such a viewpoint.

[0003]Especially, in order to correspond to the cordless making of electronic equipment, etc., the lithium cell of small lightweight and high energy density attracts attention in recent years. Since battery temperature may rise too much by misuse of an external short circuit, a surcharge, etc. in this lithium cell, Various safeguards, such as a safety valve, a PTC element (Positive Temperature Coefficient; current is intercepted when excessive current flows), and a current control circuit, are formed. Then, by becoming nonporous at a suitable temperature also to the separator used, and increasing electrical resistance, a cell reaction is stopped and the function (this is called "shutdown (SD) function".) to prevent excessive increase of temperature is called for.

[0004]As a separator suitable for such a lithium cell, Polypropylene (hereafter referred to as "PP".), and polyethylene. (It is hereafter referred to as "PE".) etc. -- the porous membrane of the polyolefine represented being used abundantly and, The mixture containing two or more sorts of resin in which the melting points, such as PP and PE, differ especially, The porous membrane of the gestalt which has a multilayer object or a concentration gradient is excellent in the characteristic, environmental aspects, cost aspects, such as SD characteristic, etc., and practicality is high (JP,4-181651,A, JP,4-206257,A, JP,6-55629,A, JP,7-216118,A, etc.).

[0005]

[Problem(s) to be Solved by the Invention]However, these separators for cells had the problem that an internal short circuit may occur, when the conductive particle powder which exfoliated from the electrode broke through the separator at the time of winding of a cell, or preservation,

since a surface consisted of soft construction material of polyolefine.

[0006]In JP,1-304933,A, it is a diameter of a surface hole of 0.05-3 micrometers, and 30 to 90% of a void content, and there is description about the polyolefine microporous film which has a coating layer which makes a subject a per [ which constitute a fine porous film / polyolefine 10g / 0.1-6g ] siloxane polymer. Although it is expectable to obtain a high mechanical strength by having such composition compared with a polyolefine independent porous membrane, Since the coverage of a polysiloxane has restriction of being the grade "which does not blockade micropore but is carrying out the tunic of the surface", it is difficult to obtain sufficient mechanical strength, and it does not come to reduce an internal short circuit defective fraction. Hot or long time is required for hardening of a polysiloxane, when an elevated temperature is used, a hole blockades by contraction of a fine porous film, and when performing prolonged hardening, a cost hike poses a problem.

[0007]This invention is excellent in a mechanical strength, especially surface hardness, and an object of this invention is to provide a porous membrane suitable for constituting the separator for nonaqueous electrolyte batteries with a small internal short circuit defective fraction at the time of battery manufacturing/storage, and such a separator.

[0008]

[Means for Solving the Problem]To achieve the above objects, the 1st gestalt of a porous membrane of this invention forms a surface protection layer which has the breathability which contains inorganic particles at least in one side of a film used as a base. By having had such composition, a mechanical strength (surface hardness) is high, When it can be considered as a porous membrane to which it splits and penetration of \*\*\*\*\* etc. does not take place easily and is used as a separator for nonaqueous electrolyte batteries, a nonaqueous electrolyte battery with a small internal short circuit defective fraction by penetration of a conductive particle at the time of battery manufacturing/storage can be provided. "It has breathability" means here that the number of Gurley seconds measured by JIS K8117 by a method of a statement is 10000 or less seconds/100 cc. In said porous membrane, it is preferred that surface hardness of a field in which a surface protection layer was

formed is more than 4H in pencil hardness, and according to this, an internal short circuit defective fraction of a nonaqueous electrolyte battery can be reduced more certainly.

[0009]In a porous membrane of this invention, it is preferred that thermal conductivity is 0.5 or more kW/m-K, and since nonporous-ization at the time of overtemperature advances promptly, the porous membrane of such composition can provide a nonaqueous electrolyte battery with high safety, when it is used as a separator.

[0010]The 2nd gestalt of a porous membrane of this invention forms a surface protection layer containing at least one resin chosen at least as one side of a film used as a base from melamine resin, urethane resin, alkyd resin, and an acrylic resin which has breathability. Surface hardness of a porous membrane can be raised by such composition as well as the 1st gestalt. It is the meaning as the above-mentioned with same "it having breathability."

[0011]According to a separator for nonaqueous electrolyte and a cell nonaqueous electrolyte battery of this invention which use a porous membrane which was mentioned above, it can be considered as a nonaqueous electrolyte battery with a small internal short circuit defective fraction at the time of battery manufacturing/storage, and high safety.

[0012]

[Embodiment of the Invention]Let the porous membrane of this invention be the porous membrane excellent in the mechanical strength by providing a surface protection layer in membranous one side or both sides used as a base.

[0013]As for the film used as a base, be [ what is necessary / just although it has porous structure ], when using the porous membrane of this invention as a separator for nonaqueous electrolyte batteries, it is preferred to use the film which has low electrical resistance and outstanding SD function. It says having the characteristics, like SD starting temperature and heat-resistant temperature with rapid electrical resistance increase at the time of SD functional expression are suitable for outstanding SD function, for example, and it is. From such a viewpoint, a suitable base is explained in this invention below.

[0014]As construction material of a base, polyolefine, polyamide, polyester, a fluoro-resin, etc. can use it conveniently. Polyolefines, such as PP and PE, are

especially preferred, and since it says that SD starting temperature and a membranous heat-resistant temperature are preferred, especially the mixture or multilayer object containing PP and PE is preferred. An antioxidant, colorant, a flameproofing agent, a bulking agent, etc. may be added to these resin.

[0015]A base has porous structure, as mentioned above, and it just uses uni-layer body or multilayer objects, such as a fine porous film, a mesh, a nonwoven fabric, textile fabrics, or foam. About 0.1-200 micrometers is suitable for it, and since the aperture of a hole has the especially quick blockade whose fine porous film which is 0.1-1.0 micrometer is a hole, it is preferred. 10000 or less seconds/100 cc of things are suitable for permeability at the number of Gurley seconds, and it is preferably made still more desirable in 1000 or less seconds/[ 100 cc and ] 2000 or less seconds/100 cc. 400 micrometers or less are suitable for the thickness of a base, and it sets 100 micrometers or less to 30 micrometers or less still more preferably preferably.

[0016]What is necessary is just to be able to form the thin film whose surface hardness is higher than a base as construction material of a surface protection layer provided in a base. The gestalt which adopted the material which includes the gestalt which adopted hereafter the material containing inorganic particles as such a material for resin of "the 1st gestalt" and the above-mentioned organic system is explained as "the 2nd gestalt."

[0017]When it is difficult to secure sufficient intensity if the thickness of a surface protection layer is too thin, it was too thick and it is used as a separator, there is a possibility of having an adverse effect on a battery characteristic.

Therefore, also in the gestalt of which [ 1st and 2nd ], it shall be appropriate for the thickness of a surface protection layer to be referred to as 0.5-100 micrometers, and it shall be 1-10 micrometers in it more preferably 1-30 micrometers. Breathability of a surface protection layer is made desirable in 2000 or less seconds/[ 100 cc and ] 10000 or less seconds/100 cc with the number of Gurley seconds.

[0018]Especially as inorganic particles used in the 1st gestalt, although it does not limit, it has hard and a light weight and a scarce thing is suitable for conductivity. As an example, they are mentioned by various metallic oxides,

metallic carbide, metal nitride, metal hydroxide, metal salt, etc., and more specifically, An aluminum oxide, a silicon dioxide, titanium oxide, a zinc oxide, tin oxide, zirconium oxide, magnesium oxide, iron oxide, copper oxide, aluminium hydroxide, silicon carbide, boron nitride, etc. are mentioned.

[0019]If the particle diameter of inorganic particles is too small, it is difficult to acquire sufficient reinforcing effect, and it is unsuitable when using it as a separator, since the total thickness of a porous membrane will become large if particle diameter is too large. Therefore, 20 micrometers or less are suitable for the mean particle diameter of inorganic particles, and it is 0.1 micrometer - 20 micrometers preferably. It is preferred that, or in the case of particles, such as fibrous, mean particle diameter shall be 0.1-10 micrometers, and average particle length shall be 1-100 micrometers.

[0020]The method of making a solvent distribute inorganic particles, and evaporating a solvent on a base, as an example of the formation method of the surface protection layer containing inorganic particles, casting, dipping, or after carrying out spray coating is mentioned. A solvent is volatility, and what does not dissolve a base and inorganic particles is preferred, for example, it can use various alcohols, water, etc., such as aromatic series, such as ketone, such as acetone, methyl ethyl ketone, and methyl isobutyl ketone, toluene, xylene, and styrene, methanol, and ethanol. Additive agents, such as a surface-active agent, may be added to the above-mentioned solvent, and, as for the rate of an additive agent, it is preferred at this time to consider it as 5 or less % of the weight.

[0021]A porous ceramic is produced with the method and conventional method which sprinkle inorganic particles on a base without using a solvent, and lamination or the method of only piling up can adopt this as a base.

[0022]As for inorganic particles, in order to improve adhesion with the base of a surface protection layer, brittleness, the ease of entering of a crack, etc., it is preferred to use it, mixing with resin used as a binder. independent [ as a binder, especially if used conventionally, it does not restrict, and / in various polyester, various polyolefines various rubbers, various acrylic resins etc. ], for example -- or it can mix and use. The mixed weight ratio of

inorganic particles and a binder makes more preferably 500 or less copies of binders [ 100 or less copies of ] 50 or less copies to 100 copies of inorganic particles. This is because it will become difficult to acquire sufficient reinforcing effect if the ratio of a binder exceeds 500 copies. A binder may harden by heating or UV irradiation.

[0023]Also as a formation method of the surface protection layer at the time of using a binder, coating methods, such as casting, dipping, or spray coating, are employable. At this time, the above solvents can also be used if needed. It is appropriate for a solvent to use it by the weight ratio of 10000 or less copies to 100 copies of inorganic particles.

[0024]When forming the surface protection layer which uses a binder with the above coating methods, permeability which was mentioned above can be secured by adjusting the concentration or coverage of coating liquid to be used. However, if coating liquid concentration or coverage is decreased in order to aim at improvement in permeability, in order that the concentration of the inorganic particles in a surface protection layer may decrease, a limit produces in membranous improving strength.

[0025]The method of forming a surface protection layer as a method of avoiding the above-mentioned problem, so that it may have puncturing like mesh state by screen-stencil is mentioned. Although the size of puncturing does not carry out limitation in particular, when using it as a separator for cells, in consideration of the size of the conductive particles leading to an internal short circuit, it shall be appropriate for it to be referred to as 0.1 micrometer - 1 mm, and it shall be 5 micrometers - 20 micrometers in it preferably. As for puncturing, it is preferred to occupy about 40 to 80% of whole surface products in the surface of a surface protection layer.

[0026]the hole to which a base has a surface protection layer in a surface protection layer by ultrasonication in the poor solvent to the resin which constitutes a surface protection layer from an above-mentioned coating method etc. after formation -- the fine pores according to structure can be formed and the above-mentioned problem can be avoided also by this method. Lower alcohol, water, etc., such as methanol, can be used as such a poor solvent.

[0027]moreover -- beforehand -- a hole -- the above-mentioned problem is also avoidable by producing the

surface protection layer which has structure and joining this to a base. For example, a porous surface protection layer is produced by extraction, extension, or addition of a foaming agent, and lamination or heavy doubling \*\*\*\*\*, the method of transferring to a base surface, after forming a surface protection layer by screen-stencil of mesh state, etc. on a releasing paper, etc. can be used for a base.

[0028]According to the desirable example of the 1st gestalt, improvement in thermal conductivity can also be aimed at as well as the improvement in the mechanical strength which is the purpose of this invention. When thinking improvement in this thermal conductivity as important, as inorganic particles to be used, an aluminum oxide, beryllium oxide, magnesium oxide, mica, etc. are preferred. When using a binder, 100 or less copies and also 50 copies or less are preferred to 100 copies of inorganic particles.

[0029]Usually, although the thermal conductivity of organic materials, such as polyethylene or polypropylene used for the separator for cells, is 0.1 - 0.3 kW/m-K alone, Since the porosity of the separator for cells is usually 40 to 50% of porous body about 10 to 90%, thermal conductivity is usually before and after 0.001 - 0.1 kW/m-K. However, according to the desirable example of this 1st gestalt, it is also possible to consider it as the thermal conductivity of 0.5 or more kW/m-K. By improvement in thermal conductivity, when it is used as a separator, speeding up of the fine-pores blockade at the time of a superfluous rise in heat can be attained, and the safety of a cell can be raised.

[0030]The porous membrane which has high thermal conductivity by porosity-ization etc. of the film which uses as a raw material polyolefines which added the lamination of A inorganic fiber nonwoven fabric and a porous membrane, B inorganic fiber, and inorganic particles other than the above-mentioned gestalt can be obtained.

[0031]In the 2nd gestalt of this invention, the resin used as a surface protection layer is melamine resin, urethane resin, alkyd resin, or an acrylic resin. Although these resin may be used independently, it is preferred to mix and use in consideration of each characteristic. As such a mixture, a mixture with melamine resin, alkyd resin, or an acrylic resin, etc. are mentioned, for example.

[0032]As a formation method of the surface protection layer in the 2nd gestalt, after applying by casting, dipping, spray



coating, etc., the method of hardening by the method according to paint film components, such as heating and UV irradiation, can be used. Additive agents other than the ingredient which forms the coat of the above-mentioned resin, such as a hardening accelerator, may be added to coating liquid. May use a solvent if needed and what does not dissolve a base for volatility is used as such a solvent, For example, ester species, such as alcohols, such as hydrocarbon, such as toluene, xylene, and hexane, methanol, and isobutyl alcohol, ethyl acetate, and isopropyl acetate, ether, terpenes, etc. can be used.

[0033]Since sufficient breathability can be secured without being able to use methods, such as ultrasonication in screen-stencil and a poor solvent, as well as the 1st gestalt that uses a binder, and restricting the quantity of a surface protection layer forming component according to these methods, it is desirable. Of course, after producing a surface protection layer independently beforehand and porosity-izing by extension etc., lamination \*\*\*\*\* etc. can be used for a base.

[0034]The above porous membranes have high surface hardness, and when it is therefore used as a separator, it splits, \*\*\*\*\* does not happen easily and they can obtain the nonaqueous electrolyte battery which is produced with a foreign matter and the internal short circuit defective fraction at the time of battery manufacturing/storage excelled [ nonaqueous electrolyte battery ] in safety small.

[0035]Such a nonaqueous electrolyte battery stores the wound type electrode body which obtained the porous membrane of a band-like negative electrode, an anode, and this invention by carrying out lamination winding to a battery can with an electrolysis solution, and is obtained by allotting other required members suitably according to a commercial cell.

[0036]As a negative pole material, what formed lithium ions, such as metal lithium, a lithium alloy, carbon, and graphite, by adsorption, the carbon material which carries out occlusion, or the conductive polymer which doped the lithium ion can be used. The graphite fluoride generally ( $\text{CF}_x$ ) shown by  $n$  as a positive electrode material, Sulfides, such as metallic oxides, such as  $\text{CoLiO}_2$ ,  $\text{MnO}_2$ , and  $\text{V}_2\text{O}_5$ ,  $\text{CuO}$ , and  $\text{Ag}_2\text{CrO}_4$ ,  $\text{TiO}_2$ , and  $\text{CuS}$ , etc. can be used. As an

electrolysis solution, ethylene carbonate, propylene carbonate, What dissolved  $\text{LiPF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ , etc. in organic solvents, such as acetonitrile, gamma-butyrolactone, 1,2-dimethoxyethane, and a tetrahydrofuran, with the electrolyte can be used.

[0037]

[Example] Hereafter, an example explains this invention in detail. However, the "part" used when the mixing ratio is expressed in the following statements means a "weight section." The characteristic of the sample was measured by the following methods.

[0038](Permeability) According to JIS K-8117, time for 10 cc of air to penetrate membrane area  $^2$  of 642 mm was measured using Yasuda energy machine factory Gurley style Denso meter No.323-Auto, and this value was increased 10 times and calculated.

[0039](Surface hardness) It asked by the pencil scratch method specified to JIS K 5400.

[0040](Thermal conductivity) A film is stuck by pressure between the heater plates of two sheets, and one heater plate is heated. After temperature became fixed, temperature-gradient  $\Delta T$  (K) and the heat transfer amount  $Q$  (cal/second) between film both sides were measured, and the thermal conductivity  $\lambda$  was computed with the following formula from thickness  $l$  of the measurement result and a film  $l$  (cm), and the area  $A$  ( $\text{cm}^2$ ).

$\lambda(\text{W/m-K}) = (Q/A) \times (l/\Delta T) \times 418.6$  [0041]

(Contraction) The film was cut off in about 10 mm in width, and length of about 300 mm so that the length direction might be in agreement with the machine direction, and it supplied for 1 hour in the hot wind circulation type dryer kept at 60 °C where this is installed by non-tension on compression paper, the length of the film before and behind heating was measured, and it asked from the percentage reduction.

[0042](Thickness) Total thickness was measured in a 1/1000-mm dial gage. The thickness of each class of a multilayer film carried out the freezing fracture of the film, and asked for it by observing a section with an optical microscope.

[0043](Example 1) PP simple substance of weight-average-molecular-weight (hereafter referred to as " $M_w$ ".)  $9.8 \times 10^5$ ,

The mixture with 50 copies of high-density PE of the 50 copies of same PP(s) and  $M_w 2.6 \times 10^5$  as this was used, and the film which has a three-tiered structure called the mixture layer/PP layer of a PP layer/PP, and PE with a three-layer T-die type film making machine was formed. At this time, extrusion temperature was 250 \*\*, the draw ratio was 30, and the total thickness of the obtained film was 32 micrometers (thickness-P layer / mixture layer / PP layer = 10/11/11 micrometer of each class). All over 25 \*\* and the clean room of 30% of relative humidity, it inserted into two 50-micrometer-thick polyethylene terephthalate films, and this film was contacted for about 10 seconds on the roll surface with a skin temperature of 150 \*\*, was heat-treated, and was rolled round on the iron core. This was supplied in a 125 \*\* dryer and heat-treated for 48 hours. Then, at 60 \*\*, this heat-treated film was extended 78% on the basis of the length of an unstretched film, and also was extended 178% on the basis of the length of an unstretched film at 120 \*\* in it (total draw magnification [ 256% of ] = 3.56 times). It is made to contract 26% on the basis of the length of the film after extension at 120 more \*\*, and let the porous membrane obtained (one 2.63 times the last draw magnification of this) be a base. To 100 copies of alumina particles (Showa Denko AL15-H) with a mean particle diameter of 3 micrometers, 50 copies of PE waxes (Mitsubishi transformation make Sun Wacks 171P), one copy of surface-active agent, and 1000 copies of xylene were added, heating stirring was performed at 100 \*\*, and the mixture was obtained. This mixture was cast at the temperature of about 80 \*\* on the base. Then, after performing ultrasonication for 2 minutes in methanol, xylene was evaporated with an 80 \*\* dryer and the porous membrane A was obtained.

[0044](Example 2) 30 copies of poly polynorbornene rubber ( no Sorex by Nippon Zeon Co., Ltd.) and 1000 copies of xylene were added to 100 copies of silica particles with a mean particle diameter of 1.2 micrometers, heating stirring was performed at 60 \*\*, and the mixture was produced.

Spray spraying of this mixture was performed by amount of superintendent officers 5 g/m<sup>2</sup> on the base produced like Example 1, desiccation of 2 hours was performed at 90 \*\* after that, and the porous membrane B was obtained.

[0045](Example 3) To the mean fiber diameter of 0.3-0.6 micrometer, and 100 copies of 10-20 micrometers of mean

fiber length's fibrous potassium titanate particles ( TISMO-D D by Otsuka Chemical Co., Ltd.), 100 copies of polyester resin ( Byran 630 by Toyobo Co., Ltd.), 250 copies of toluene and 100 copies of methyl isobutyl ketone were added, the ball mill performed stirring for 24 hours, and the mixture was obtained. On the base produced like Example 1, this mixture was cast at ordinary temperature. Then, after performing ultrasonication for 2 minutes in methanol, the solvent was evaporated in a 120 °C dryer and the porous membrane C was obtained.

[0046](Example 4) 90 copies of liquid paraffins were added to the mixture of two copies of ultrahigh-molecular-weight PE of  $M_w 2.5 \times 10^6$ , and eight copies of PE of  $6.8 \times 10^5$ , and the solution of PE constituent was obtained. this solution 100 weight section -- 2,6-t-butyl-p-cresol ("BHT".) 0.125 copy and 0.25 copy of tetrakis [methylene- 3 -(3,5-di-t-butyl-4-hydroxyphenyl)- propionate] methane by Sumitomo Chemical Co., Ltd. ("IRUGA NOx 1010", Ciba-Geigy make) were added as an antioxidant, and it mixed.

Autoclave with an agitator was filled up with this mixture, and the uniform solution was obtained. While this solution was extruded from the T die with the extruder and the cooling roller took over, the gel upper sheet was fabricated. The obtained sheet was set to the biaxial-stretching machine, and the said biaxial stretching was increased 7x7 times by a part for temperature [ of 115 °C ], and stretching speed/of 0.5 m. After carrying out extraction removal of the liquid paraffin which washes the obtained extension film with a methylene chloride, and remains, it dried and the base which is a monolayer porous membrane of PE was obtained. The mixture produced like Example 1 on this base was cast at the temperature of about 80 °C. Then, after performing ultrasonication for 2 minutes in methanol, xylene was evaporated with an 80 °C dryer and the porous membrane D was obtained.

[0047](Example 5) The porous membrane E was obtained by the same method as Example 2 except having used the base produced like Example 4.

[0048](Example 6) The porous membrane F was obtained by the same method as Example 3 except having used the base produced like Example 4.

[0049](Example 7) Ultraviolet curing type 100 copies of acrylic urethane system oligomer and three copies of

benzophenones were melted in 400 copies of ethyl acetate, and high speed stirring was performed. On the base produced like Example 1, this mixture was cast at ordinary temperature. After evaporating ethyl acetate, with the high-pressure mercury lamp, the optical exposure was carried out, curing treatment was carried out by addition light volume  $150 \text{ mJ/cm}^2$ , and the porous membrane G was obtained.

[0050](Example 8) The porous membrane H was obtained by the same method as Example 7 except having used the base produced like Example 4.

[0051]The result measured about the characteristic of porous membrane A-H obtained in the above-mentioned example is shown in Table 1. The result of having performed measurement respectively same as the samples I and J for the base of Examples 1 and 4 which do not form the surface protection layer as a comparative example is indicated collectively.

[0052]

[Table 1]

Sample	Permeability	Surface hardness	Thermal conductivity
Contraction (a second /100cc)	(pencil hardness)	(kW/m-K)	(%)
A 900 4H 0.9 2.0	B850 4H 0.8 1.9	C1000 5H 0.7 2.0	D. 800 3H 0.9 1.0
E 750 4H 0.7 1.1	F 900 5H 0.6 1.3	G 1200 2H 0.12 2.1	H 1400 3H 0.14 1.1
I 800 H 0.08 2.3	J 700 HB 0.1 1.2		

[0053]It produced 1000 lithium ion batteries at a time respectively, using porous membrane A-H as a separator. Inter-electrode resistance of each cell was measured and the rate that what is below  $2\text{k}\Omega$  exists was made into the internal short circuit defective fraction.

[0054]Similarly it prepares respectively ten lithium ion batteries using the porous membranes A-H as a separator at a time. The peg test was done based on the method specified to a Battery Association of Japan indicator SBA G 1101 "lithium secondary battery safety-parameters guideline", and it was considered as the defective fraction depended for \*\*\*\*(ing) the number of a cell with a burst and ignition.

[0055]Measurement respectively same as the samples I and J was performed for the base of Examples 1 and 4 which does not form the surface protection layer as a comparative example. The internal short circuit defective fraction and the defective fraction depended for \*\*\*\*(ing) in each sample are shown in Table 2.

[0056]

[Table 2]

Sample Internal short circuit defective fraction Defective  
fraction (%) by \*\*\*\* A (piece / 10 piece) 0.5 Zero B0.6  
0C0.4 0D0.4 Zero E0.5 Zero F0.3 0G 0.7 Zero H0.5 0I2.3  
4J 1.1 1[0057]

[Effect of the Invention]As explained above, according to  
the porous membrane of this invention, it can be considered  
as a porous membrane with high surface hardness by  
forming the surface protection layer which contains at least  
in one side of the film used as a base inorganic particles or  
resin which was mentioned above. By using it for a  
nonaqueous electrolyte battery by making such a porous  
membrane into a separator, The inconvenience that the  
conductive particle which exfoliated from the electrode  
material at the time of production of a cell or preservation  
penetrates a separation can be reduced, and it can be  
considered as the nonaqueous electrolyte battery excellent in  
the safety to which generating of an internal short circuit  
does not take place easily as a result.

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